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Climatic and pedoclimatic factors driving C and N dynamics in soil and surface water in the alpine tundra (NW-Italian Alps)

Michele Freppaz[1,2], Davide Viglietti[1,2], Raffaella Balestrini[3], Michele Lonati[1], Nicola Colombo[1,2]

1 *Department of Agricultural, Forest and Food Sciences, University of Torino, Largo Paolo Braccini 2, 10095 Grugliasco (TO), Italy* **2** *Research Center on Natural Risk in Mountain and Hilly Environments, NatRisk, University of Torino, Largo Paolo Braccini 2, 10095 Grugliasco (TO), Italy* **3** *Water Research Institute (IRSA-CNR), Via del Mulino 19, 20861 Brugherio (MB), Italy*

Corresponding author: *Michele Freppaz* (michele.freppaz@unito.it)

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Abstract

In alpine tundra the interannual and seasonal variability of C and N forms in soil and lake water during the short snow-free season could be significant and related to climatic and pedoclimatic variables. The hypothesis that not only the climatic and pedoclimatic parameters recorded during the summer season but also the ones measured during the previous snow-covered season could contribute to explaining the C and N dynamics in soil and surface water was tested along 10 snow-free seasons in 3 sites in the alpine tundra in the north-western Italian Alps (LTER site Istituto Mosso). Among the considered parameters, the snow cover duration (SCD) exerted a primary control on soil N-NH_4^+, DOC, C_{micr}, N_{micr} and DOC:DON ratio, with an inverse relationship. A long SCD might cause the consumption of all the subnival substrata by the soil microorganisms, determining a C starvation during the subsequent snow-free season. An opposite trend was observed for the lake water, where a longer SCD corresponded to a higher content of inorganic N forms. Among the pedoclimatic indices, the number of soil freeze/thaw cycles (FTC) recorded during the snow-covered season had a positive relation with most of soil C and N forms and N-NO_3^- in lake

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water. Only the soil DON showed an inverse pattern, and this result is consistent with the hypothesis that FTC released soil DON, subsequently decomposed and mineralized. Only N-NO_3^- had a significant intraseasonal variability, reaching the highest values in September both in soil and water, revealing a significant slowdown of the contribution of soil N immobilization processes.

Keywords
LTER, snow cover duration, soil temperature, freeze/thaw cycles, leaching, N-NO_3^-

Introduction

The alpine tundra is a high-mountain environment located above the tree-line, which occurs across a wide range of latitudes and landscapes with common properties such as: a short growing season, extended periods with air temperature below freezing, and long periods with snow-covered soils (Edwards et al. 2007, Knowles et al. 2015). Since snow controls soil organic matter decomposition and nitrogen (N) release (Walker et al. 1999, Groffman et al. 2001), variations in the depth and duration of snow cover result in large differences in pedoclimatic conditions and nutrient cycling, as well as in plant community composition (Walker et al. 1993, Fisk et al. 1998). Direct control involves the effects of snow cover on winter soil temperature by insulating soil from air temperature and/or on summer soil moisture. Indirect control involves the effects of snow cover variations on growing-season length and soil nutrients dynamics (Edwards et al. 2007).

Several studies performed in other ecotones, such as the boreal forests, demonstrated that the climatic conditions of the preceding winter are important driving factors of the C cycling during the growing season (e.g. Öquist and Laudon 2008, Haei et al. 2013). Consequently, not only the climatic and pedoclimatic conditions recorded during the growing season (e.g. soil temperature and moisture) can strongly affect the soil nutrient cycling, but also those of the previous winter season (e.g. snow cover duration, number of soil freeze/thaw cycles).

Although organic matter decomposition may be slow, the decomposition below the snowpack may still constitute a significant proportion of the total decomposition because the snow-covered season is long (Stark 2007). A thick snow cover usually maintains the soil temperature close to 0 °C throughout the snow-covered season, with significant microbial processes which could be influenced by the occurrence of freeze/thaw cycles, especially during the spring and autumn. The effects of freeze-thaw cycles may strongly depend on the number of cycles, the duration of the freezing period, and the minimum temperature (Grogan et al. 2004, Freppaz et al. 2007). After freeze/thaw events there is a significant flush of microbial respiration, most probably because soil microorganisms that die during the event represent an easily decomposable and nutrient-rich substrate for the surviving microorganisms (Schimel and Clein 1996, Herrmann and Witter 2002). Freeze/thaw events may release nutrients from the soil microbial biomass and/or through aggregates breakdown (Freppaz et al. 2007), being major drivers of nutrient mobilization in tundra systems. Research outcomes from a variety of forest and alpine ecosystems have shown increased mobilization of nitrate

associated with soil freezing, including sites in U.S. (Mitchell et al. 1996, Brooks et al. 1998), Germany (Callesen et al. 2007), and Japan (Christopher et al. 2008).

Snowmelt- and rainfall-driven leachate of nitrate is a key hydrochemical feature in montane catchments and has been studied extensively in order to understand its underlying mechanisms and ecological consequences (Stottlemyer 1992, Campbell et al. 2000, Sickman et al. 2003, Harms and Jones 2012). Soil characteristics and water pathways within soils are decisive for the nutrient transport from terrestrial to aquatic ecosystems. Water can be transported laterally through subsurface soil layers to streams or lakes (Khalili et al. 2010) and a variety of studies have found stream dissolved organic carbon (DOC) to be correlated with soil organic C and N (e.g. Houser et al. 2006) and allochthonous DOC (produced in the catchment and not in the lake itself) to represent the larger fraction of the total DOC in lakes (Sobek et al. 2007). Other studies have described a negative relationship between the export of nitrate and soil C:N ratios (e.g. Lovett et al. 2002).

In subarctic streams and rivers, higher inorganic N concentrations have been measured during the late growing season and fall (Petrone et al. 2006), suggesting a greater soil nutrient leaching during these periods potentially playing an important role in annual nutrient export. Alpine basins should not be considered as "teflon basins" since surface-groundwater interactions are a fundamental component of water quantity and quality even in areas with bedrock or talus deposits (Williams et al. 1997, Campbell et al. 2000).

Although much is known in the alpine tundra about litter decomposition, soil C and N cycling and microbial communities under the snowpack and during the period of snow melting (e.g. Brooks and Williams 1999, Baptist et al. 2010), less is known about the contribution of the pedoclimatic factors recorded during the snow-covered season on the soil N and C forms of the subsequent snow-free season. Our time series of soil N and C forms collected in the alpine tundra during the growing season under naturally changing snow cover characteristics (e.g. snow cover duration, cumulative snowfall), climatic (e.g. liquid precipitation) and pedoclimatic conditions (e.g. soil temperature) can provide information about the influence of these environmental factors on soil processes and water lake characteristics and the interactions between them. Our main goal was to quantify the influence of climate and pedoclimate factors on soil and lake water C and N cycling, examining the contribution of snow-covered conditions on the subsequent growing season. Given the general sensitivity of soil nutrient cycling in this ecosystem we expected that even small changes in these factors could significantly affect the soil C and N dynamics both on an interannual and seasonal basis.

Methods

Study area

The research area (Long Term Ecological Research [LTER] site Angelo Mosso Scientific Institute) is located in NW Italy (Piemonte Region), close to the Monte Rosa

Massif (4634 m a.s.l.), along the border with the Valle d'Aosta Region (Fig. 1). The study was conducted at three high-elevation research sites 1, 3, and 5, at elevations equal to 2840, 2770 and 2525 m a.s.l., respectively. The sites are located in the upper part of a glacial valley. The bedrock mineralogy is primarily micaschists, with some inclusions of ophiolites and calcschists. Soils are classified as Skeletic Dystric Regosol (site 1), Skeletic Umbrisol (Arenic) (site 3), and Skeletic Dystric Cambisol (site 5) (IUSS Working Group WRB, 2015). Soil total organic C (TOC) and N (TN) ranged from 6.5 to 75.0 g kg^{-1} and from 0.5 to 5.1 g kg^{-1}, respectively; soil pH ranged from 4.4 to 5.4 (Freppaz et al. 2010, Magnani et al. 2017a,b). In the years 2009, 2010, 2014, 2016, and 2017, the mean snow density before snowmelt onset was equal to 316 kg m^{-3}, while the $N\text{-}NH_4^+$ and $N\text{-}NO_3^-$ stocks in the snowpack ranged between 0.24–0.82 and 0.53–2.92 kg ha^{-1}, respectively.

All the three study sites are ascribable to the 'Siliceous alpine and boreal grasslands' (habitat 6150, according to the EU Habitat Directive), but a large between-site difference in plant species composition was observed according to contrasting extremes of exposure and snow cover duration. Site 1 was a typical snow-bed community belonging to the *Salicion herbaceae* phytosociological alliance. Site 3 was an alpine microthermal *Carex curvula*-dominated grassland, ascribable to the *Caricion curvulae* alliance. Site 5, located at the lowest altitude, was dominated by *Agrostis schraderiana* Bech. (*Festucion variae* alliance).

Among the research sites, site 1 was located within the basin of the alpine lake Cimalegna, as shown in Figure 1. The Cimalegna Lake basin was delineated using a digital terrain model-DTM (cell size: 10×10m) produced by Regione Piemonte. The Cimalegna Lake basin covers an area of approximately 4.4 ha and is characterized by 35% rocks and 65% vegetated soil (Magnani et al. 2017b). The lake area was equal to 2700 m^2 and the max water depth was about 3.4 m. Further physical and chemical features of Cimalegna Lake are reported in Magnani et al. (2017b).

Although the Alpine Permafrost Index Map (APIM) (Boeckli et al. 2012) indicates high probability of permafrost presence in the basin (mean permafrost index > 0.8), the basin does not have permafrost because of the large presence of relatively well evolved soil with vegetation and massive bedrock outcrops, which are generally considered as indicating factors of warm conditions and/or permafrost absence.

Climatic and pedoclimatic measurements

Air temperature, liquid precipitation (during the snow-free season), and snowfall have been continuously recorded since 2005 by an Automatic Weather Station (AWS) located at 2901 m a.s.l. and belonging to the Italian Army (Comando Truppe Alpine – Ufficio Meteomont) (Fig. 1). At each research site, thermistors combined with data loggers (GEOTEST UTL-1, instrument sensitivity: ± 0.1 °C) were placed at a soil depth of 10 cm from fall 2007 until fall 2017 for the measurement of hourly soil temperature.

To assess the climatic conditions in the area, several indices were extracted from the AWS data (listed and described in Table 1): (i) cumulative snowfall (CS); (ii)

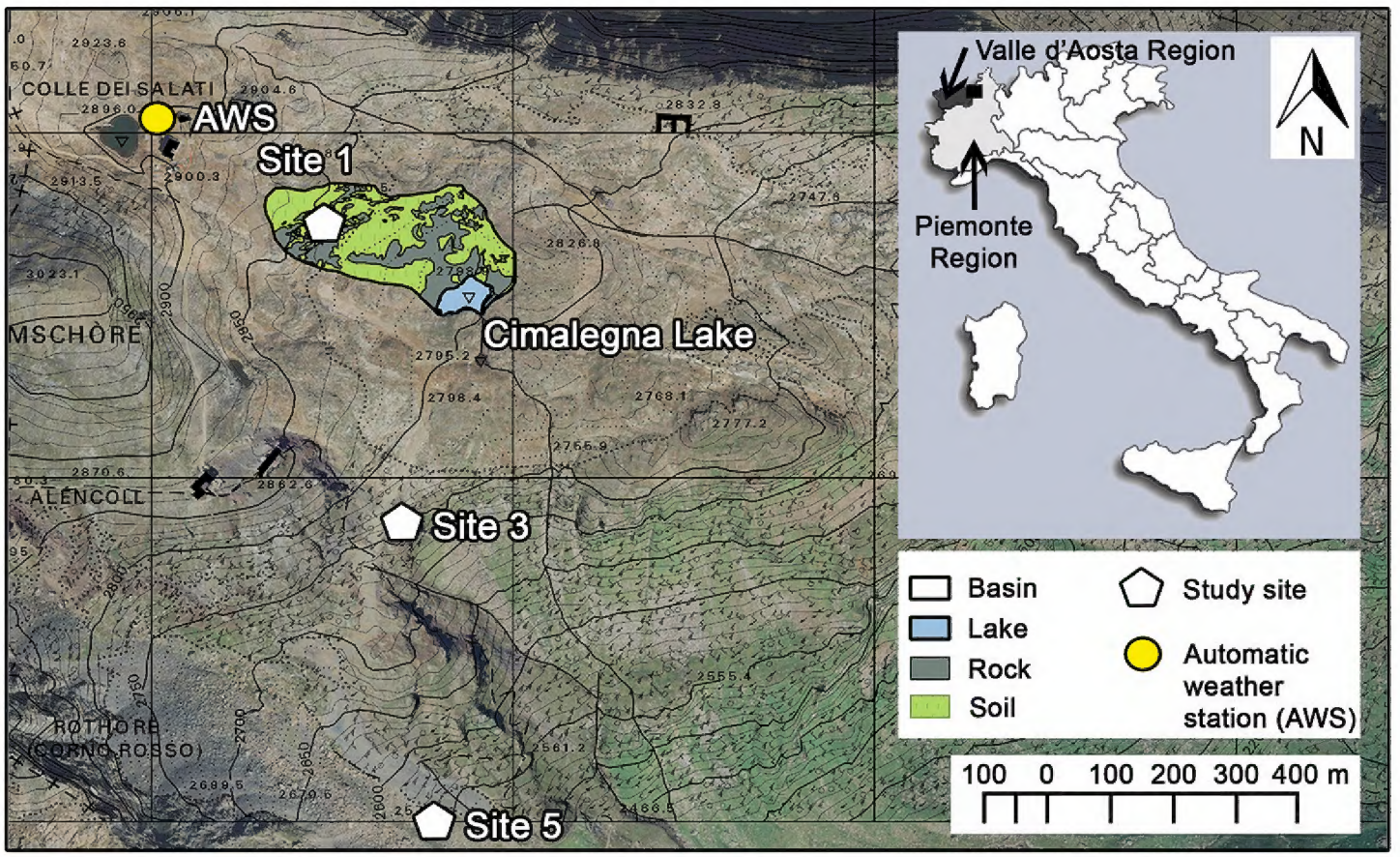

Figure 1. Localization of the study area in Italy, Cimalegna Lake basin and lake, soil sampling sites (1, 3 and 5), and the automatic weather station (AWS). Rock and soil land cover categories refer to the selected basin area of Cimalegna Lake.

heavy precipitation days (HPD); (iii) very heavy precipitation days (VHPD); (iv) consecutive wet days (CWD); (v) consecutive dry days (CDD). Moreover, to assess the site-specific pedoclimatic conditions, further indices were calculated (listed and described in Table 1): (i) snow cover duration (SCD), calculated from 1 October to 30 September (hydrological year) on the basis of the daily soil temperature data. When the daily soil temperature amplitude remained within a range of 1 °C, the day was defined as a "snow-covered day" (Danby and Hik 2007); (ii) melt-out day of snow (MOD); (iii) duration of soil freezing (DSF); (iv) soil freeze/thaw cycles (FTC), considered when the daily mean soil temperature dropped below and rose above 0 °C (Phillips and Newlands 2011); (v) mean soil temperature during the freezing period (MTF); (vi) mean soil temperature during the snow-covered season (MTSC); (vii) mean soil temperature during the snow-free season (MTSF); (viii) intensity of soil freezing (ISF). As suggested by Tierney et al. (2001), ISF was classified as "mild freezing", "mild/hard freezing" or "hard freezing" when the daily mean soil temperature ranged between 0 and -5 °C, -5 and -13 °C, or lower than -13 °C, respectively.

Soil and lake water sampling and analysis

Each soil study site consisted of three plots, each 9 m^2. From 2008 until 2010, once a year at the end of the snow-free season (September), and from to 2011 to 2017, monthly during the snow-free season, three topsoil samples (A horizon, 0–10 cm depth) were

Table 1. Indices used to assess the influence of climatic and pedoclimatic conditions on C and N forms in soil and water (adapted from Tiwari et al. 2018). * Melt-out day of snow (MOD) and snow cover duration (SCD) are considered pedoclimatic indices since they were calculated from soil temperature data.

Index	Term	Definition	Unit
Climatic index			
Cumulative snowfall	CS	Cumulative daily fresh snow calculated for each hydrological year (1 October to 30 September)	cm
Heavy precipitation days	HPD	Number of days, between samplings, when daily liquid precipitation >10 mm. For the first sampling the considered period is between melt-out day and sampling day	days
Very heavy precipitation days	VHPD	Number of days, between samplings, when daily liquid precipitation >20 mm. For the first sampling the considered period is between melt-out day and sampling day	days
Consecutive wet days	CWD	Maximum number of consecutive days, between samplings, when precipitation >1mm. For the first sampling the considered period is between melt-out day and sampling day	days
Consecutive dry days	CDD	Maximum number of consecutive days, between samplings, when precipitation <1mm. For the first sampling the considered period is between melt-out day and sampling day	days
Pedoclimatic index			
Snow cover duration*	SCD	Sum of "snow-covered days" in each hydrological year	days
Melt-out day of snow*	MOD	Date of complete snowmelt (indicated as day of the year - DOY)	DOY
Duration of soil freezing	DSF	Cumulative number of days, from October 1 to the melt-out day, when mean daily soil temperature <0 °C	days
Soil freeze/thaw cycles	FTC	Number of soil freeze/thaw cycles in each hydrological year	number
Mean soil temperature during soil freezing	MTF	Mean daily soil temperature when the soil is frozen, from October 1 to the melt-out day	°C
Mean soil temperature during the snow-covered season	MTSC	Mean daily soil temperature when the soil is snow-covered	°C
Mean soil temperature during the snow-free season	MTSF	Mean daily soil temperature between samplings. For the first sampling the considered period is between melt-out day and sampling day	°C
Intensity of soil freezing	ISF	Minimum soil temperature when soil is frozen	°C

collected, which in turn consisted of three subsamples in each plot. Soil samples were homogenized by sieving at 2 mm within 24 h of collection. At each sampling time, subsamples were dried at 100 °C overnight in order to obtain the gravimetric water content. An aliquot of 20 g of fresh soil was extracted with 100 mL K_2SO_4 0.5 M, whereas a 10 g aliquot was subjected to chloroform fumigation for 18 h before extraction with 50 mL K_2SO_4 0.5 M. Dissolved organic carbon (DOC) was determined with 0.45 μm membrane, which filtered K_2SO_4 extracts (extractable DOC) with a TOC analyzer (Elementar, Vario TOC, Hanau, Germany). Microbial carbon (Cmicr) was calculated from the difference in DOC between fumigated and non-fumigated samples corrected by a recovery factor of 0.45 (Brookes et al. 1985). Ammonium (extractable $N\text{-}NH_4^+$) concentrations in soil extracts were determined spectrophotometrically (U-2000, Hitachi, Tokyo, Japan) by a modified Berthelot method involving reaction with salicylate in the presence of alkaline sodium dichloroisocyanurate (Crooke and Simpson 1971). Nitrate (extractable $N\text{-}NO_3^-$) concentrations in soil extracts were de-

termined spectrophotometrically (U-2000, Hitachi, Tokyo, Japan) by the Greiss reaction as described by Mulvaney (1996) and modified by Cucu et al. (2014). Total dissolved nitrogen (TDN) in the extracts was determined as reported for DOC. Dissolved organic nitrogen (extractable DON) was determined as the difference between TDN and inorganic nitrogen ($N\text{-}NH_4^+ + N\text{-}NO_3^-$) in the extracts. Microbial nitrogen (Nmicr) was calculated from the difference in TDN between fumigated and non-fumigated samples corrected by a recovery factor of 0.54 (Brookes et al. 1985). Total nitrogen and total carbon were determined by elemental analysis (Carlo-Erba, Milano, Italy). A total of 267 soil samples were analyzed in the time-span 2008–2017.

Lake water was sampled approximately at the same time that soil was sampled, with a total of 79 samples analyzed in the time-span 2008–2017. The lake was sampled from 3 points on the shore with no vegetation, at ca. 10-cm depth. Shore samples were assumed not to be significantly different from mid-lake samples because the investigated lake was small and shallow (Mast et al. 2011). The analyses were performed in the laboratory on filtered samples (0.45 μm) within 48 h from the sampling. Ammonium ($N\text{-}NH_4^+$) concentrations in lakes were determined spectrophotometrically (U-2000, Hitachi, Tokyo, Japan) by a modified Berthelot method involving reaction with salicylate in the presence of alkaline sodium dichloroisocyanurate (Crooke and Simpson 1971). Nitrate ($N\text{-}NO_3^-$) concentrations in the water samples were determined spectrophotometrically (U-2000, Hitachi, Tokyo, Japan) by the Greiss reaction as described by Mulvaney (1996) and modified by Cucu et al. (2014). Since 2011, DOC was determined after filtering the water samples with a 0.45 μm membrane by a TOC analyzer (Elementar, Vario TOC, Hanau, Germany). Total dissolved nitrogen (TDN) was determined as reported for DOC. Dissolved organic nitrogen (DON) was determined as the difference between TDN and inorganic nitrogen ($N\text{-}NH_4^+ + N\text{-}NO_3^-$).

Statistical analyses

In order to assess the interannual variability in C and N forms in soils and lake water in the time-span 2008–2017, only the samples collected at the end of the snow-free season (September) were considered (during the first 3 years the sampling was carried out only during September), while for the evaluation of the intraseasonal variability, the monthly samples (July, August, September, October) were considered. We tested significant differences among years and months by one-way ANOVA and Bonferroni post hoc test ($p < 0.05$). Data were previously tested for homoscedasticity (Levene's test) and for normality (Kolmogorov–Smirnov test), and transformed when necessary.

In order to describe the variation of climatic and pedoclimatic indices over the 10 studied years, a Principal Component Analysis (PCA) was performed using all the variables described in Table 1 and calculated from the AWS (climatic indices) and from the data loggers in each site (pedoclimate indices). Climatic and pedoclimatic variables recorded during the winter seasons were referred to the measurement periods as follows: e.g.winter 2007–2008 was year 2008, winter 2008–2009 was year 2009, etc.

The influence of climatic and pedoclimatic variables on C and N forms in soil was evaluated by fitting generalized linear models (GLMs). Soil C and N forms were used as dependent variables and a gamma distribution was used because normality (tested with Kolmogorov-Smirnoff test) was not met (Zuur et al. 2009). Climatic and pedoclimatic variables (Tab. 1) were used in the models as explanatory variables. Highly collinear predictors ($r > |0.70|$) were excluded after a Pearson correlation analysis. Explanatory variables were standardized (Z-scores) to allow for analysis of effect size by scrutinizing model parameters (β coefficients). In order to evaluate the influence of climatic, pedoclimatic and soil properties on C and N forms in lake water, a similar GLM procedure was performed, using water properties as dependent variables and adding soil variables (from Site 1) as predictors.

All the statistical analyses were performed using SPSS v.19 (SPSS 2010).

Results

Climatic and site-specific pedoclimatic conditions

The mean annual air temperature measured at the AWS in the time-span 2008–2017 was -2.3 °C, with mean daily values ranging from a minimum of -21.1 °C (16 January 2017) to a maximum of +12.4 °C (24 August 2016) (Fig. 2a). The cumulative liquid precipitation during the snow-free season ranged between 285 mm in 2010 and 374 mm in 2015, with a maximum accumulated daily liquid precipitation of 103.8 mm (10 August 2015). The maximum snow depth was equal to 560 cm (28 April 2009). CS ranged from 605 cm in winter 2008 to 1099 cm in winter 2009 (Tab. 2). HPD ranged from 2 in 2014 to 12 in 2008, while VHPD comprised between 0 in 2014 and 7 in 2015 and 2016. The minimum number of CWD was 3 in 2009, while the maximum was 9 in 2016. CDD ranged between 5 in 2010 and 23 in 2014.

Soil temperature measured at all study sites during the snow-covered season was generally close to 0 °C (Fig. 2b). During the snow-covered season, the daily topsoil temperature ranged between a minimum of -8.3 °C in 2013 at site 3, while during the snow-free season it reached the maximum of 17.2 °C at site 5 in 2016. SCD was comprised between 210 (site 3, 2015) and 286 (site 1, 2014) (Tab. 3). The SCD resulted strongly positively correlated with the MOD ($r=0.88$, $p < 0.001$). Earliest MOD occurred at site 3 and 5 on DOY 139 (2011) while latest MOD occurred at site 1 on DOY 221 (2009). DSF ranged between 0 (site 5, 2015) and 269 (site 1, 2010). The maximum number of FTC (4) was measured at sites 3 and 5 in 2008. Lowest MTF (-1.6 °C) occurred at site 3 in 2013. Lowest MTSC (-1.6 °C) was measured at site 3 in 2012. Lowest MTSF was 4.5 °C at site 1 (2014). Conversely, the highest MTSF was 11.3 °C at site 5 (2009). ISF was always classified as mild freezing, except for 2 events of mild/hard freezing recorded at site 3 in 2013 (-8.3 °C) and in 2016 (-7.4 °C) (cf. Tierney at al. 2001).

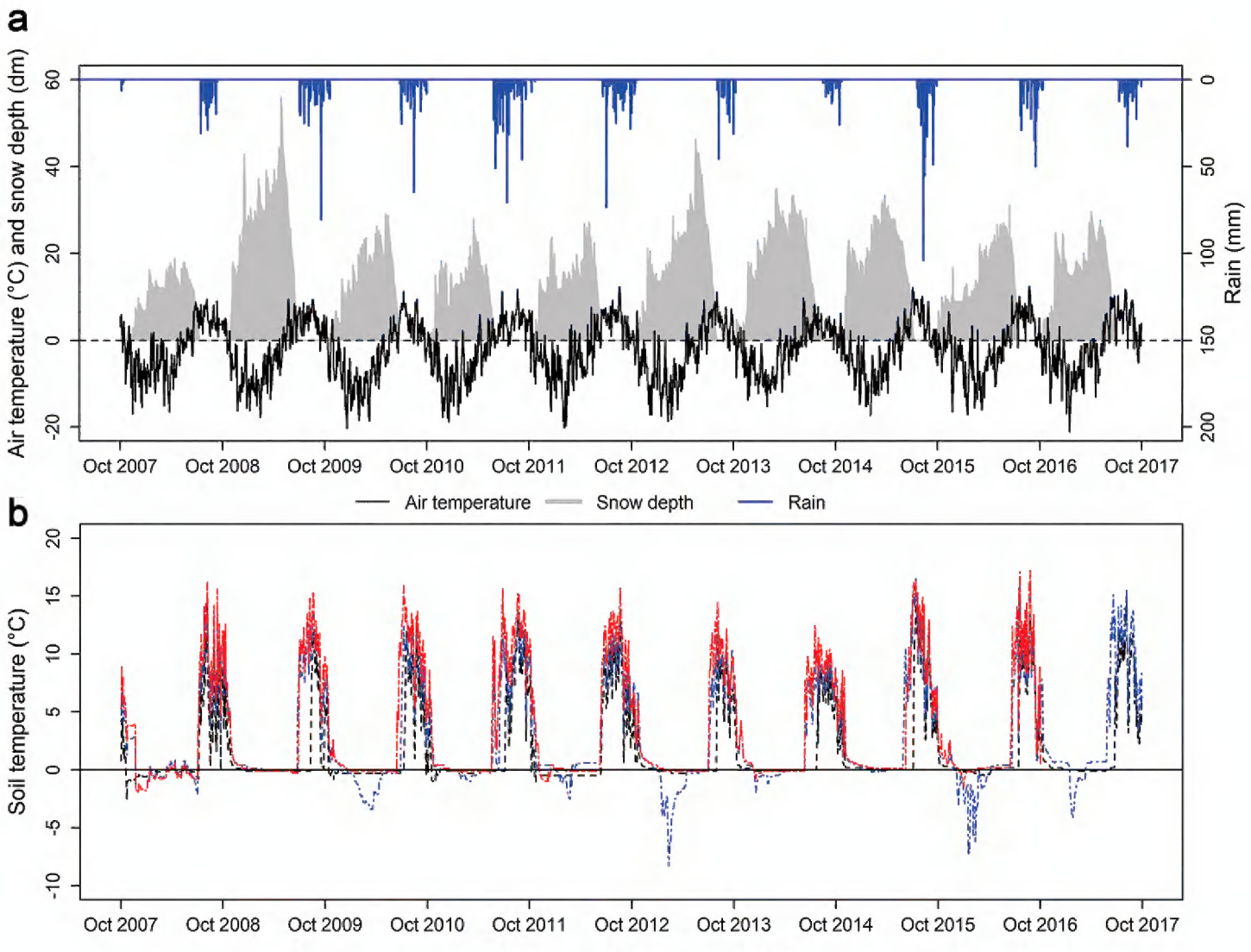

Figure 2. a Air temperature, snow depth and rain recorded at the Automatic Weather Station (AWS) from 1 October 2007 to 30 September 2017 (daily mean values) **b** soil temperature recorded in the topsoil (A horizon – 10 cm depth) at study sites 1, 3, and 5 (daily mean values).

Table 2. Climatic indices derived from the AWS data. CS (cumulative snowfall), HPD (heavy precipitation days), VHPD (very heavy precipitation days), CWD (consecutive wet days), and CDD (consecutive dry days). All indices are listed and described in Table 1.

Index	Unit	2008	2009	2010	2011	2012	2013	2014	2015	2016	2017	Min	Max	Mean	St.dev
CS	cm	605	1099	879	752	890	947	820	820	756	608	605	1099	817	150
HPD	days	12	5	5	3	8	5	2	5	6	6	2	12.0	5.7	2.8
VHPD	days	4	2	2	4	4	3	0	7	7	3	0	7	4	2
CWD	days	7	3	6	4	4	7	5	7	9	6	3	9	6	2
CDD	days	18	9	5	9	6	5	23	12	9	16	5	23	11	6

The PCA revealed the distribution of the years in three different groups (Fig. 3). The year 2008 was characterized by a high number of FTC and very low MTF, ISF and MTSC. The years 2011, 2012, 2015 and 2017 were characterized by the earliest MOD and the shortest SCD, while the years 2009, 2010, 2013, 2014 and 2016 were characterized by the longest SCD.

Table 3. Site-specific pedoclimate indices measured at sites 1, 3, and 5 between 2008 and 2017. SCD (snow cover duration*), MOD (melt-out day of snow*), DSF (duration of soil freezing), FTC (soil freeze/thaw cycles), MTF (mean soil temperature during soil freezing), MTSC (mean soil temperature during the snow-covered season), MTSF (mean soil temperature during the snow-free season), and ISF (intensity of soil freezing). All indices are listed and described in Table 1. * SCD and MOD are considered a pedoclimatic index since they were calculated on the basis of the soil temperature data.

Index	Unit	2008	2009	2010	2011	2012	2013	2014	2015	2016	2017	Min	Max	Mean	St.dev
Site 1															
SCD	days	249	272	271	255	241	284	286	250	283	262	241	286	265	16
MOD	DOY	181	221	192	187	163	211	205	186	193	175	163	221	191	17
DSF	days	205	246	269	208	235	217	223	15	102	124	15	269	184	79
FTC	number	3	1	3	1	2	1	1	1	1	1	1	3	2	1
MTF	°C	-0.3	-0.1	-0.1	-0.4	-0.5	-0.1	0.0	0.0	-0.3	-0.1	-0.5	0.0	-0.2	0.2
MTSC	°C	-0.3	0.0	-0.3	-0.2	-0.5	-0.1	0.0	0.1	0.0	0.1	-0.5	0.1	-0.1	0.2
MTSF	°C	5.8	8.5	7.6	7.2	6.8	5.1	4.5	9.0	7.7	6.4	4.5	9.0	6.9	1.4
ISF	°C	-2.6	-0.1	-0.8	-0.3	-1.1	-0.3	-0.1	0.0	-0.5	-0.1	-2.6	0.0	-0.6	0.8
Site 3															
SCD	days	222	246	222	219	223	247	231	210	274	228	210	274	232	19
MOD	DOY	182	174	179	139	162	184	162	148	188	146	139	188	166	18
DSF	days	167	125	211	154	58	184	125	59	122	57	57	211	126	55
FTC	number	4	1	2	2	2	1	1	1	1	1	1	4	2	1
MTF	°C	-1.0	-0.1	-1.1	-0.3	-0.9	-1.6	-0.5	-0.1	-0.9	-1.6	-1.6	-0.1	-0.8	0.6
MTSC	°C	-0.1	0.1	-0.8	-0.1	0.1	-1.1	-0.3	0.2	-0.6	0.2	-1.1	0.2	-0.3	0.4
MTSF	°C	8.1	10.0	9.1	8.5	8.3	6.6	7.2	10.0	6.5	9.1	6.5	10.0	8.3	1.3
ISF	°C	-2.1	-0.1	-3.4	-1.0	-2.5	-8.3	-1.9	-0.2	-7.4	-4.1	-8.3	-0.1	-3.1	2.8
Site 5															
SCD	days	219	244	235	219	216	253	235	222	248		216	253	232	14
MOD	DOY	183	178	164	139	160	182	161	157	165		139	183	165	14
DSF	days	190	156	176	147	163	160	181	0	68		0	190	138	63
FTC	number	4	1	1	1	1	1	1	0	1		0	4.0	1.2	1.1
MTF	°C	-0.7	-0.1	-0.1	-0.1	-0.5	-0.1	-0.1		-0.3		-0.7	-0.1	-0.2	0.2
MTSC	°C	-0.1	0.0	0.0	0.0	0.0	0.2	0.0	0.3	0.2		-0.1	0.3	0.1	0.1
MTSF	°C	9.2	11.3	10.8	9.3	9.7	7.8	8.4	10.8	6.5		6.5	11.3	9.3	1.6
ISF	°C	-1.9	-0.3	-0.3	-0.3	-0.1	-0.1	-0.8		-1.4		-1.9	-0.1	-0.7	0.7

Influence of climatic and pedoclimatic variables on C and N forms in soil

On the interannual basis, the N-NO_3^- concentration was significantly higher in years 2008, 2009 and 2010, while the lowest values were recorded in years 2014, 2016 and 2017 (Fig. 4a). Conversely, the mean soil N-NH_4^+ concentration was rather constant among the years, with the exception of year 2010 (Tab. 4). The lowest soil extractable DON concentration was recorded between 2008 and 2011, while the highest value was measured in 2013. The DOC concentration was rather stable through years, with the exception of 2010. The highest DOC:DON ratio was measured in the years 2008, 2009, 2010 and 2011. The lowest microbial C concentration was recorded in the years 2013, 2014, 2015, 2016 and 2017, while the maximum was recorded in 2012. The highest microbial N concentration was measured in 2008. The highest C: Nmicr was measured

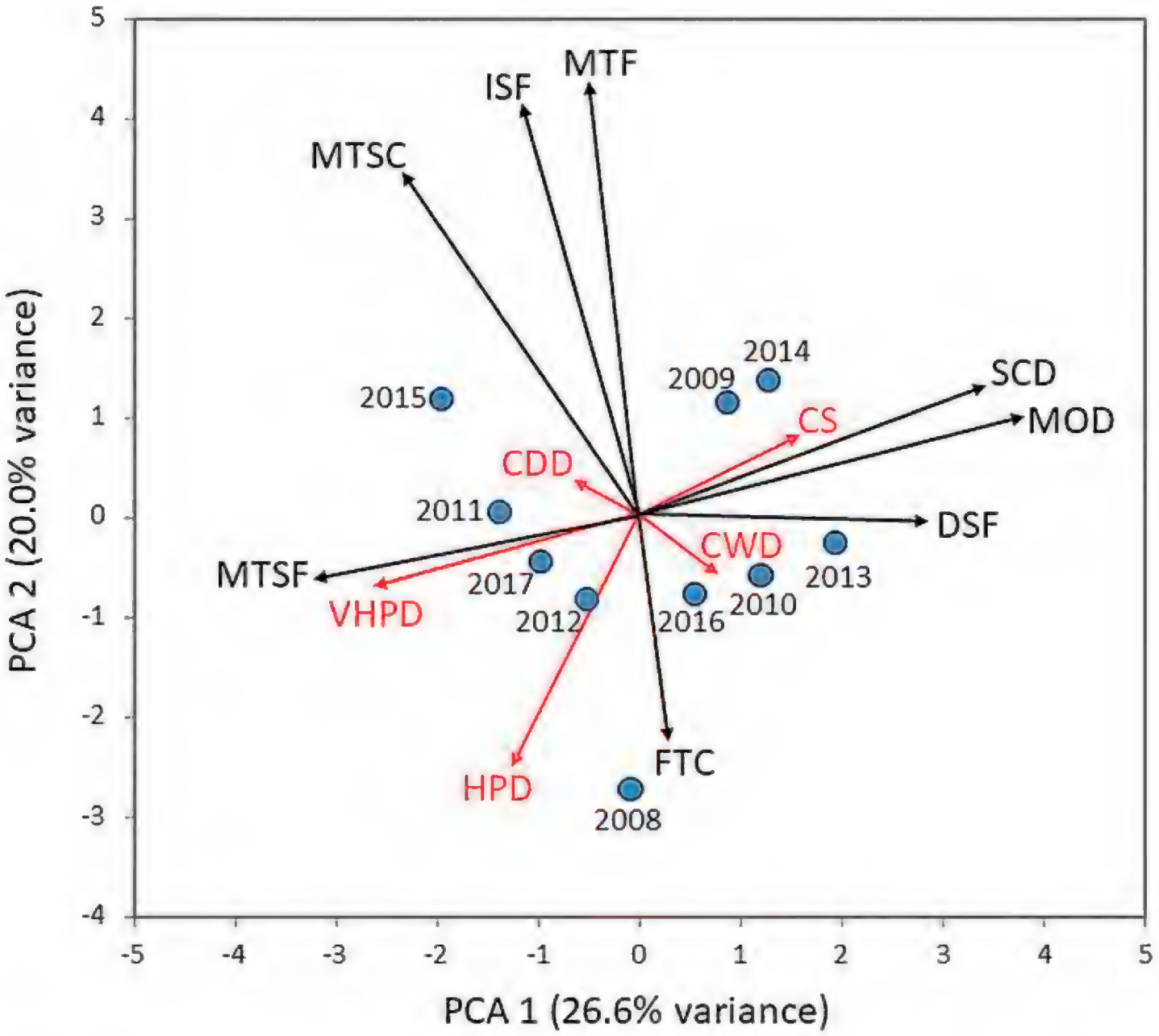

Figure 3. Principal Component Analysis showing the variation of climatic (red arrows) and pedoclimatic (black arrows) indices over the 10 studied years. Blue points represent the average coordinates of different sampling date and replicates within the same year. Descriptions for each climate and pedoclimate index can be found in Table 1.

in years 2011 and 2012, while the lowest was in 2014. On a seasonal basis, $N\text{-}NO_3^-$ concentration significantly increased in September (Fig. 4b), while there were not significant differences between months in all the C and N forms considered in the study (Tab. 4).

All soil C and N forms were positively correlated with CS, with the exception of the microbial C:N ratio that was inversely correlated (Tab. 5). HPD was positively correlated with $N\text{-}NO_3^-$ concentration, while VHPD was inversely correlated with DON. CWD was inversely correlated with $N\text{-}NH_4^+$, Cmicr and Nmicr while CDD was inversely correlated with the microbial C:N ratio (Tab. 5). Considering the site-specific indices, SCD was the main driving factor for the concentration of $N\text{-}NH_4^+$, DOC, Cmicr and Nmicr, which were all inversely correlated with SCD, as well as $N\text{-}NO_3^-$, TDN and Cmicr:Nmicr. DSF was positively correlated with $N\text{-}NH_4^+$, Cmicr and the Cmicr:Nmicr,

Table 4. Mean interannual and seasonal concentrations of N-NH_4^+, N-NO_3^-, DOC, TDN, Cmicr, Nmicr, DON (mg kg^{-1}), and values of C:Nmicr and DOC:DON at the 3 study sites in years 2008–2017. Letters represent significant differences between years and months ($p < 0.05$), letters are not reported when differences are not significant ($p > 0.05$).

Parameter	2008	2009	2010	2011	2012	2013	2014	2015	2016	2017	Min	Max	Mean	St.dev
Interannual														
N-NH_4^+	9.9 (B)	9.7 (B)	21.2 (A)	6.9 (B)	6.9 (B)	5.4 (B)	4.5 (B)	5.1 (B)	2.2 (B)	4.4 (B)	2.2	21.2	7.6	5.3
N-NO_3^-	2.6 (B)	7.3 (A)	5.9 (A)	0.4 (BC)	1.0 (BC)	0.9 (BC)	0.2 (C)	1.2 (B)	0.2 (C)	0.2 (C)	0.2	7.3	2.0	2.5
DOC	324.2 (B)	308.2 (B)	576.5 (A)	251.7 (B)	335.7 (B)	302.6 (B)	212.0 (B)	365.6 (AB)	164.9 (B)	180.7 (B)	164.9	576.5	302.2	117.9
TDN	30.8 (AB)	32.7 (AB)	24.0 (B)	8.2 (C)	32.5 (AB)	61.9 (A)	39.7 (AB)	44.5 (AB)	34.8 (AB)	36.4 (AB)	8.2	61.9	34.5	13.8
Cmicr	2178.4 (B)	1150.4 (BC)	1769.1 (BC)	2106.5 (AB)	3029.8 (A)	872.3 (C)	1001.1 (C)	944.7 (C)	729.2 (C)	760.1 (C)	729.2	3029.8	1454.2	777.1
Nmicr	228.4 (A)	110.6 (AB)	102.7 (B)	67.3 (B)	98.5 (B)	64.4 (B)	135.7 (AB)	78.2 (B)	44.6 (B)	35.4 (B)	35.4	228.4	96.6	55.6
DON	18.3 (B)	16.1 (B)	6.7 (B)	4.4 (B)	32.4 (AB)	55.5 (A)	35.0 (AB)	38.8 (AB)	32.3 (AB)	31.7 (AB)	4.4	55.5	27.1	15.7
C:Nmicr	12.2 (BC)	11.0 (C)	19.4 (BC)	55.5 (B)	42.9 (A)	25.2 (BC)	8.1 (C)	12.2 (BC)	16.7 (BC)	21.1 (BC)	8.1	55.5	22.4	15.3
DOC:DON	17.6 (B)	24.5 (A)	41.5 (A)	33.7 (A)	11.0 (BC)	5.2 (C)	6.5 (BC)	11.7 (BC)	5.5 (C)	7.7 (BC)	5.2	41.5	16.5	12.8
	Jul	**Aug**	**Sep**	**Oct**	**Min**	**Max**	**Mean**	**St.dev**						
Seasonal														
N-NH_4^+	6.0	6.8	7.8	6.2	6.0	7.8	6.7	0.8						
N-NO_3^-	0.6 (A)	0.6 (A)	1.9 (B)	1.0 (A)	0.6	1.9	1.0	0.7						
DOC	299.9	271.6	303.7	258.2	258.2	303.7	283.4	22.0						
TDN	30.8	32.7	24.0	8.2	8.2	32.7	23.9	11.1						
Cmicr	1476.9	1066.6	1482.7	1276.7	1066.6	1482.7	1325.7	197.5						
Nmicr	104.3	107.7	100.8	90.5	90.5	107.7	100.8	7.4						
DON	30.6	39.5	29.2	31.3	29.2	39.5	32.7	4.6						
C:Nmicr	17.4	21.5	21.7	29.9	17.4	29.9	22.6	5.3						
DOC:DON	17.7	11.0	12.5	12.7	11.0	17.7	13.5	2.9						

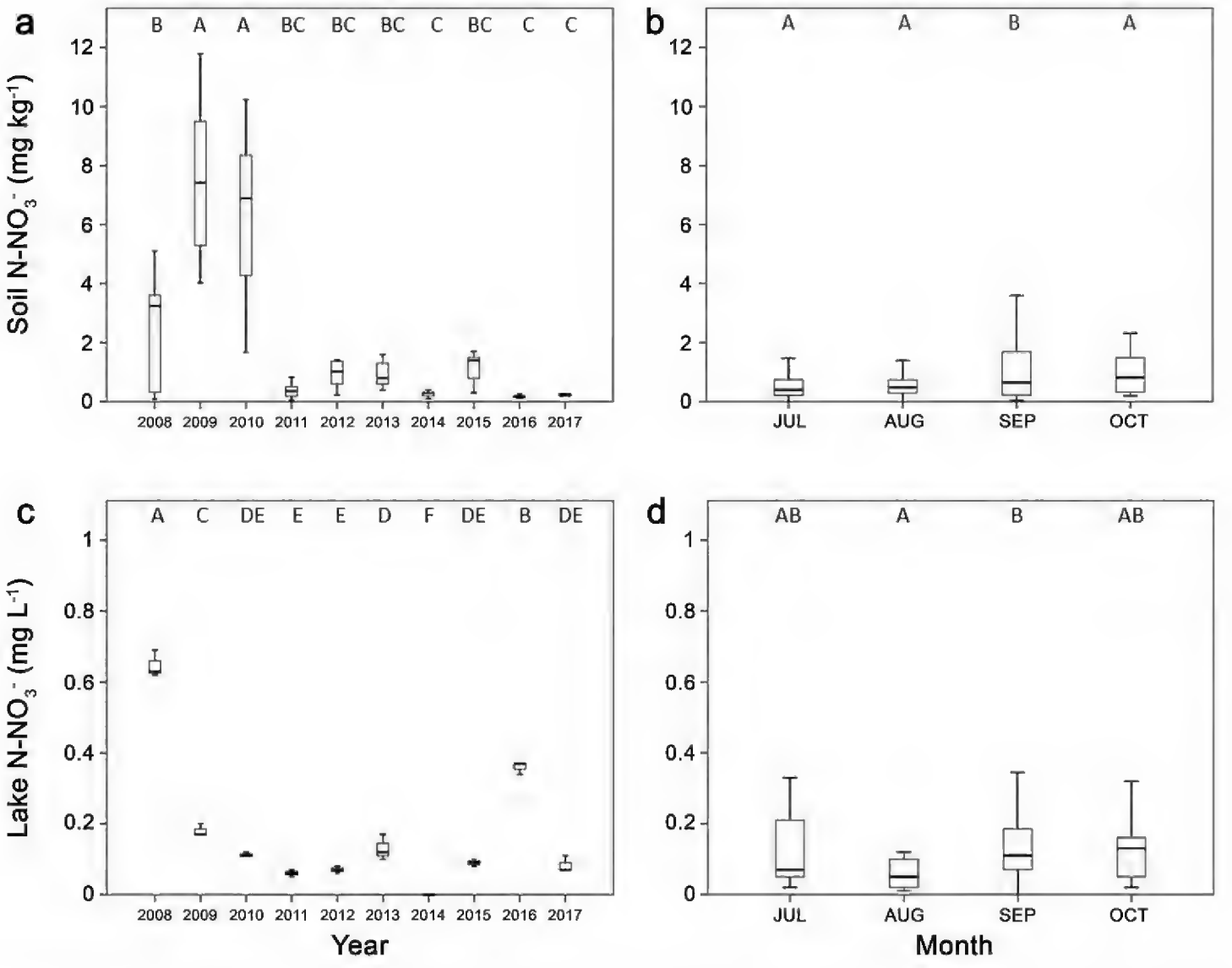
a
b
c
d
Soil N-NO3- (mg kg-1)
Lake N-NO3- (mg L-1)
B A A BC BC BC C BC C C
A A B A
A C DE E E D F DE B DE
AB A B AB
2008 2009 2010 2011 2012 2013 2014 2015 2016 2017
JUL AUG SEP OCT
Year
Month

Figure 4. a Mean extractable soil nitrate ($N\text{-}NO_3^-$) concentrations (mg kg^{-1}) recorded in September at the three study sites in the time-span 2008–2017 (n = 87, in 2017 the site 5 was not sampled) **b** mean seasonal concentration $N\text{-}NO_3^-$ (mg kg^{-1}) in the 3 study sites in years 2008–2017 **c** mean water nitrate ($N\text{-}NO_3^-$) (mg L^{-1}) concentration recorded in September at the Cimalegna Lake during the years 2008–2017 (n = 30) **d** Mean seasonal concentration (mg L^{-1}) of $N\text{-}NO_3^-$ at the Cimalegna Lake in years 2008–2017 (n = 30). Upper-case letters represent significant differences between years and months ($p < 0.05$).

while it was negatively correlated with DON. In the latter case this parameter was the most influential among the considered variables. Also FTC had a significant influence on $N\text{-}NH_4^+$, $N\text{-}NO_3^-$, DOC, Cmicr, Nmicr and DON. All these C and N forms were positively correlated with the exception of DON. MTF was negatively correlated with TDN, DON and the Cmicr:Nmicr ratio, while it was positively correlated with Nmicr. MTSC was positively correlated only with the Cmicr:Nmicr ratio (Tab. 5).

Influence of climatic, pedoclimatic and soil properties on C and N forms in lake water

On an interannual basis, the maximum $N\text{-}NO_3^-$ concentration in water was recorded in 2008, while the lowest was measured in 2011 and 2012 (Fig. 4c). The highest $N\text{-}NH_4^+$ values were recorded in 2008 and 2010 (Tab. 6). The highest DOC and

Table 5. Results of generalized linear models (GLMs) showing the effects of climatic and pedoclimatic variables on soil C and N forms. Explanatory variables were standardized (Z-scores) to allow for analysis of effect size by scrutinizing model parameters (β coefficients). *p*-values are also shown.

Predictor	$N\text{-}NH_4^+$		$N\text{-}NO_3^-$		DOC		TDN		Cmicr		Nmicr		DON		C:Nmicr		DOC:DON	
	β	*p*	β	*p*	β	*p*	β	*p*	β	*p*	β	*p*	β	*p*	β	*p*	β	*p*
Climatic index																		
CS	**0.19**	**0.000**	**0.43**	**0.000**	**0.25**	**0.000**	**0.33**	**0.000**	**0.11**	**0.004**	**0.26**	**0.000**	**0.31**	**0.000**	**-0.13**	**0.014**	**-0.25**	**0.001**
HPD	-0.02	0.772	**0.37**	**0.000**	-0.02	0.575	**0.13**	**0.029**	0.08	0.134	0.11	0.155	0.14	0.083	0.04	0.566	**-0.35**	**0.002**
VHPD	0.07	0.225	0.10	0.340	0.06	0.141	**-0.14**	**0.019**	0.10	0.077	-0.06	0.477	**-0.18**	**0.018**	0.08	0.306	-0.02	0.835
CWD	**-0.14**	**0.018**	-0.20	0.053	-0.05	0.226	-0.02	0.783	**-0.13**	**0.037**	**-0.21**	**0.016**	-0.03	0.722	0.13	0.159	-0.05	0.711
CDD	0.03	0.473	-0.04	0.516	0.01	0.621	0.01	0.106	-0.07	0.100	0.08	0.111	0.04	0.486	**-0.22**	**0.000**	**-0.32**	**0.000**
Pedoclimatic index																		
SCD	**-0.38**	**0.000**	**-0.32**	**0.000**	**-0.39**	**0.000**	**-0.09**	**0.042**	**-0.45**	**0.000**	**-0.33**	**0.000**	-0.06	0.307	**-0.21**	**0.001**	**-0.62**	**0.000**
DSF	**0.14**	**0.010**	0.00	0.646	0.02	0.656	**-0.28**	**0.000**	**0.15**	**0.009**	-0.13	0.117	**-0.31**	**0.000**	**0.52**	**0.000**	**0.45**	**0.000**
FTC	**0.13**	**0.015**	**0.20**	**0.014**	**0.12**	**0.001**	-0.07	0.164	**0.12**	**0.007**	**0.23**	**0.002**	**-0.17**	**0.011**	-0.09	0.238	0.05	0.614
MTF	-0.02	0.685	0.06	0.481	-0.03	0.481	**-0.21**	**0.001**	-0.04	0.523	**0.18**	**0.032**	**-0.22**	**0.004**	**-0.31**	**0.000**	**0.37**	**0.002**
MTSC	0.00	0.991	-0.16	0.082	-0.03	0.509	0.04	0.484	0.01	0.210	-0.13	0.116	0.00	0.693	**0.33**	**0.000**	0.09	0.445
MTSF	0.05	0.277	-0.07	0.351	-0.01	0.753	-0.05	0.285	0.02	0.620	-0.03	0.606	-0.01	0.902	0.00	0.968	-0.15	0.177

Table 6. Mean interannual and seasonal concentrations of $N\text{-}NH_4^+$, $N\text{-}NO_3^-$, DOC, TDN, DON (mg L^{-1}), and values of DOC:DON at the Cimalegna Lake. Letters represent significant differences between years and months ($p < 0.05$), letters are not reported when differences are not significant ($p > 0.05$).

Parameter	2008	2009	2010	2011	2012	2013	2014	2015	2016	2017	Min	Max	Mean	St.dev
Interannual														
$N\text{-}NH_4^+$	0.2 (B)	0.0 (C)	0.3 (A)	0.0 (C)	0.0 (C)	0.0 (C)	0.0 (C)	0.0 (C)	0.0 (C)	0.0 (C)	0.0	0.3	0.1	0.1
$N\text{-}NO_3^-$	0.6 (A)	0.2 (C)	0.1 (DE)	0.1 (E)	0.1 (E)	0.1 (D)	0.0 (F)	0.1 (DE)	0.4 (B)	0.1 (DE)	0.0	0.6	0.2	0.2
DOC				2.5 (A)	1.6 (B)	0.7 (C)	1.2 (BC)	1.5 (B)	1.6 (B)	1.1 (BC)	0.7	2.5	1.5	0.6
TDN				0.7 (A)	0.4 (B)	0.2 (CD)	0.2 (CD)	0.3 (C)	0.5 (B)	0.2 (D)	0.2	0.7	0.4	0.2
DON				0.6 (A)	0.3 (B)	0.1 (CD)	0.2 (C)	0.3 (B)	0.1 (D)	0.1 (D)	0.1	0.6	0.2	0.2
DOC:DON				4.3 (B)	5.6 (B)	6.8 (B)	6.0 (B)	6.1 (B)	19.7 (A)	18.3 (A)	4.3	19.7	9.5	6.5
	Jul	**Aug**	**Sep**	**Oct**	**Min**	**Max**	**Mean**	**St.dev**						
Seasonal														
$N\text{-}NH_4^+$	0.0	0.0	0.1	0.0	0.0	0.1	0.0	0.0						
$N\text{-}NO_3^-$	0.1 (AB)	0.1 (A)	0.2 (B)	0.1 (AB)	0.1	0.2	0.1	0.1						
DOC	1.7	1.8	1.4	1.5	1.4	1.8	1.6	0.2						
TDN	0.5	0.4	0.4	0.4	0.4	0.5	0.4	0.1						
DON	0.3	0.3	0.2	0.2	0.2	0.3	0.3	0.1						
DOC:DON	6.3	6.6	10.5	6.7	6.3	10.5	7.5	2.0						

DON concentrations were recorded in 2011, while the highest DOC:DON ratio was observed in 2016 and 2017. On a seasonal basis, the lowest N-NO_3^- concentration was recorded during August, while the maximum was in September (Fig. 4d). The N-NH_4^+ concentration did not show any significant difference between months, as reported for DOC and DON (Tab. 6).

Among the selected climatic indices, CS was inversely correlated with N-NH_4^+ (Tab. 7). VHPD was inversely correlated with the concentration of N-NH_4^+ and DON, while CWD was positively correlated with N-NH_4^+ and DOC. CDD was inversely correlated with N-NO_3^-. Considering the site-specific indices (site 1), SCD was positively correlated with N-NH_4^+, as FTC. DSF was inversely correlated with the DOC:DON ratio, while MTF was inversely correlated with DOC and DON. MTSF was positively correlated with the DOC:DON ratio. Among the soil C and N forms, the concentration of N-NH_4^+ in soil was inversely correlated with the N-NH_4^+ concentration in lake, as TDN and DON, while it was positively correlated with the DOC:DON ratio. The concentration of N-NO_3^- in soil was positively correlated with the N-NO_3^- concentration in lake, while it was inversely correlated with the DOC:DON ratio. The concentration of DOC in soil was positively correlated with N-NH_4^+, DOC, TDN and DON in water. The Cmicr was positively correlated with N-NH_4^+ and the DOC:DON ratio. The soil microbial N was positively correlated

Table 7. Results of generalized linear models (GLMs) showing the effects of climatic, pedoclimatic and soil variables on water C and N forms. Explanatory variables were standardized (Z-scores) to allow for analysis of effect size by scrutinizing model parameters (β coefficients). *p*-values are also shown.

Predictor	N-NH_4^+		N-NO_3^-		DOC		TDN		DON		DOC:DON	
	β	*p*	β	*p*	β	*p*	β	*p*	β	*p*	β	*p*
Climatic index												
CS	**-0.32**	**0.023**	0.15	0.342	-0.02	0.760	-0.02	0.756	-0.09	0.460	0.07	0.536
HPD	0.07	0.684	0.24	0.201	0.03	0.744	-0.07	0.352	0.12	0.419	-0.11	0.359
VHPD	**-0.72**	**0.000**	0.01	0.950	-0.01	0.831	0.00	0.966	**-0.19**	**0.008**	0.11	0.115
CWD	**0.46**	**0.003**	0.28	0.060	**0.13**	**0.038**	0.12	0.061	0.09	0.434	-0.01	0.883
CDD	-0.19	0.161	**-0.38**	**0.000**	0.08	0.168	-0.01	0.924	0.07	0.466	-0.11	0.173
Pedoclimatic index												
SCD	**1.07**	**0.000**	**0.59**	**0.029**	-0.06	0.689	-0.02	0.922	-0.25	0.379	0.35	0.160
DSF	-0.24	0.120	-0.37	0.106	-0.02	0.878	0.11	0.307	0.26	0.154	**-0.38**	**0.029**
FTC	0.27	0.372	**0.59**	**0.046**	-0.25	0.313	**-0.54**	**0.028**	-0.69	0.134	0.31	0.447
MTF	0.21	0.156	**-0.38**	**0.023**	**-0.21**	**0.022**	**-0.51**	**0.000**	**-0.44**	**0.004**	0.13	0.359
MTSF	0.12	0.424	-0.24	0.071	0.03	0.675	-0.06	0.392	-0.15	0.193	**0.30**	**0.003**
Soil parameter												
S_N-NH_4^+	0.16	0.404	**0.47**	**0.023**	-0.12	0.228	-0.06	0.528	-0.19	0.211	0.23	0.124
S_N-NO_3^-	**-0.25**	**0.047**	**0.43**	**0.000**	-0.13	0.210	0.04	0.712	0.21	0.223	**-0.48**	**0.001**
S_DOC	**0.49**	**0.006**	0.25	0.078	**0.17**	**0.007**	**0.22**	**0.001**	**0.27**	**0.010**	-0.12	0.229
S_Cmicr	**0.43**	**0.009**	0.28	0.253	0.13	0.288	-0.02	0.886	-0.35	0.111	**0.64**	**0.001**
S_Nmicr	-0.38	0.082	**-0.49**	**0.046**	0.04	0.727	0.00	0.984	**0.43**	**0.041**	**-0.60**	**0.001**
S_DON	-0.24	0.075	-0.15	0.356	**-0.17**	**0.026**	-0.09	0.232	-0.08	0.560	-0.17	0.129
S_C:Nmicr	0.00	0.982	**-0.30**	**0.021**	0.00	0.966	-0.09	0.158	0.18	0.116	-0.23	0.049
S_DOC:DON	-0.26	0.053	**-0.42**	**0.009**	**0.08**	**0.299**	-0.05	0.478	0.03	0.831	-0.08	0.477

with DON, while it was inversely correlated with the DOC:DON ratio. The soil DON was inversely correlated with DOC in water, while the soil Cmicr:Nmicr ratio was inversely correlated with N-NO_3^- and DOC:DON ratio in soil.

Discussion

Influence of climatic and pedoclimatic variables on C and N forms in soil

Along the study period, the climate and pedoclimate conditions showed a great interannual variability, with some extreme meteorological events. For example, in 2008, the little and delayed snowpack accumulation and consequently the low insulation exerted by the snowpack caused a high number of soil FTC in all sites. In high-elevation ecosystems, the most frequent periods for FTC are spring and fall, when the soil cannot be covered by a consistent snowpack. Sometimes they can also occur throughout the winter, due to little snowpack accumulation and/or the wind action that causes a snow removal exposing the soil to cold air temperature (Hiemstra et al. 2002), as observed in winters 2013 and 2016, when soil mild/hard-freezing was recorded in site 3. FTC could damage the biological tissue of the microorganisms, resulting in the death of the soil microbial biomass, with the release of nutrients that are potentially immobilized by the surviving microorganisms (Brooks et al. 1995, Larsen et al. 2002). FTC may also have a disruptive effect on soil aggregation due to ice formation, which can result in "fresh" reactive surfaces becoming exposed, causing an increase in nutrient availability (Freppaz et al. 2007).

In our research sites, the resulting FTC number recorded during the snow-covered season significantly and positively correlated with the concentrations of most of the soil C and N forms in the subsequent growing season (cf. Haei et al. 2010). The only exception was DON, which was inversely correlated to FTC. FTC can damage or kill microbes, returning microbial protein and cell walls to the organic matter pool, while releasing amminoacids and other organic monomers into the DON pool (Schimel and Bennett 2004). This pool could be mineralized during the subsequent growing season, with a significant release of inorganic N forms (Grogan et al. 2004). As reported by Haei et al. (2010), in our study the increase in soil DOC pool was related to the number of FTC, revealing how changes in the insulation properties of the snow cover (e.g. little and delayed snowpack accumulation in late fall) may significantly affect the soil thermal status and consequently the biogeochemical processes during the winter, with consequence for DOC formation and export. As reported by Fuss et al. (2016), our results are consistent with soil frost causing a physical disruption of the soil matrix that resulted in the prolonged release of DOC for several months after the melting of snow rather than as a single pronounced pulse. The higher the number of FTC, the higher also the release of soil nitrate. This pattern is not consistent with the hypothesis that when soil freezing mobilizes DOC, the increased DOC availability can enhance microbial immobilization of NO_3^- and reduces losses (e.g. Groffman et al. 2001, Fuss et al. 2016).

The duration and intensity of soil freezing during the snow-covered season was positively related to an increase in the soil and microbial C:N ratio, suggesting the prevalence of fungi, characterized by a higher C:N ratio in comparison to bacteria. Lipson et al. (2002) reported that in an alpine dry grassland fungi are dominant in winter and more adapted to cold temperatures than bacteria, with a shift in structure and function between winter and summer.

In the time-span considered in this study, the interannual variability of the SCD and melt-out day was marked and it was possible to discriminate years with short and long snow-cover duration, which corresponded to early and late melt-out days, respectively. According to the conceptual model of Brooks and Williams (1999), our research area could be included in a transition zone between Zone II and Zone III, where small changes in SCD could have significant effects on the number of soil FTC and on the soil N and C dynamics (Magnani et al. 2017a). In particular, based on the weight of the variables in the GLM models, we showed that SCD had a first order control on the interannual variability of soil $N\text{-}NH_4^+$, $N\text{-}NO_3^-$, DOC, Cmicr, Nmicr and the DOC:DON ratio. Due to a deep snow cover soils seldom froze in the study area during fall, winter and spring (cf. Sickman et al. 2001). The soil temperature generally remained close to 0 °C, favoring the subnival decomposition processes and therefore the gradual consumption of organic substrate due to microorganism respiration (Lipson et al. 2000). A similar effect was reported for forest sites at a lower elevation (Schindlbacher et al. 2014). A number of studies reported a substantial decrease in subnival soil substrate availability from early to late winter (e.g. Zimov et al. 1996, Brooks et al. 2004) when Cmicr limitation increased, as inputs from plant litter were depleted. The winter-adapted microbial community ultimately succumbed to warmer temperatures and C starvation during spring thaw (Lipson et al. 2000).

Among the climatic indices, the cumulative snowfall was positively related to all the soil C and N forms. We assume that a higher cumulative snowfall in the study area corresponded to a higher soil water content and nutrient inputs into the soil during the spring melting of snow, enhancing the microbial activity and the C and N transformations. In the same area, Magnani et al. (2017a) reported a positive correlation between the soil water content and the microbial biomass. Soil moisture is commonly considered one of the main factors regulating the microbial activity during the growing season. In an alpine ecosystem, Lipson et al. (1999) reported the minimum level of soil microorganisms in correspondence to the lowest level of soil moisture during the growing season, underlying the controlling action of the soil moisture on soil microorganisms through a direct osmotic effect or through a diffusive effect on the availability of the substrate.

In contrast to what was found by Magnani et al. (2017a), the mean soil temperature recorded during the snow-free season (~7 °C) was not related to any of the soil C and N forms, and this could be the cause of their reduced seasonal changes. This is consistent with other studies in alpine meadows which found little evidence of impact of the pedoclimatic conditions on the DOC dynamics, in favor of biotic factors (e.g. quality of the ground and belowground biomass) (e.g. Luo et al. 2009).

Influence of climatic and pedoclimatic variables, and soil on C and N forms in water

A number of studies have demonstrated that some physical features of the catchment strongly influence the chemical composition of surface water, and may control ecosystem responses to global perturbations, such as changes in climate (Clow and Sueker 2000, Sickman et al. 2002, Lewis 2002, Kopácek et al. 2005, Helliwell et al. 2007, Balestrini et al. 2013). In particular, Balestrini et al. (2013) reported that in some North America and European high-elevation catchments, the areal extensions of developed soils are inversely related to nitrate concentrations in surface waters. Analogously, Helliwell et al. (2007) indicated the fundamental role that the soil biological community plays in the retention and loss of N and therefore the strict connection between soil and waters in mountain remote ecosystems.

In our study the resultant $N\text{-}NO_3^-$ content in lake water positively correlated with the soil inorganic N forms. This concurs with the findings of Magnani et al. (2017b) that investigated the relationships between soil and water C and N forms in the same area but for a shorter time-span (2013–2015). These authors found a significant positive correlation between the nitrate concentration in soil and the nitrate concentration in lake water, revealing how the temporal variation of $N\text{-}NO_3^-$ observed in the lake strictly reflected the temporal changes occurring in the soils (Campbell et al. 2002). We did not find any correlation between the rainfall patterns and the $N\text{-}NO_3^-$ content in lake water. The reason could be that although in our study area we may expect that large summer storms can have a notable influence on surface water chemistry, in our GLM analysis we considered the sum of the rainfall events between the water samplings. Therefore we could not assess the potential contribution of the closest rainfall episodes to the water sampling time. This is in accordance with the fact that chemical responses to rain events during the summer are generally transient (Clow et al. 2003). A general increase in solute concentrations in lake was generally found during the fall as the relative importance of subsurface soils inputs to lakes increase and uptake of nitrogen by vegetation declines. During the warmer months, biological uptake and denitrification processes in the soils likely prevailed and led to a decrease in $N\text{-}NO_3^-$ export. This is in accordance with the inverse relationship that we found between soil microbial N and $N\text{-}NO_3^-$ content in water, revealing the importance of soil microbial N immobilization in limiting the leaching processes. During the fall, biological mediated immobilization processes slowed down with the result of $N\text{-}NO_3^-$ rise in lake water and soil, a pattern in our study area especially evident in September, and reported also in the western United States mountains (NWT LTER site) where nitrate, dissolved organic carbon and nitrogen flushed from soils to streams (Williams et al. 2015). In our study area we found an increase in $N\text{-}NO_3^-$ concentration both in soils and water especially during September, but in lake water also in July, revealing in this case a potential contribution of the snow melting through the ionic pulse phenomenon (e.g. Sickman et al. 2003).

As reported for the soil matrix, the number of FTC had an important control on the $N\text{-}NO_3^-$ content in lake water and, as reported by Fitzhugh et al. (2001), it is

possible to hypothesize a strong N-NO_3^- leaching response to soil frost. The soil temperature experienced during soil freezing events is usually not cold enough to directly kill roots, therefore a physical disruption of the soil matrix (e.g. frost heaving) may contribute to the fine root mortality and consequently to a reduced N uptake by plants (Fuss et al. 2016).

The SCD had a first order control on N-NH_4^+ and N-NO_3^- concentration in water, but an opposite pattern was observed in comparison to soil C and N forms. A longer SCD caused an increase of both N-NH_4^+ and N-NO_3^- concentrations in the lake water, which could be related to the reduction of the microbial nutrient immobilization processes in soil. In our study DOC concentration in water was positively related to the DOC concentration in soil, revealing how allochthonous DOC could represent a large fraction of the total DOC in lakes (Sobek et al. 2007), leached from terrestrial soils. The amount of DOC released from soils is determined by the production of leachable organic carbon in soils and by the water yield. Indeed, the CWD was found to influence the C forms both in soil and water, causing a decrease in the soil microbial biomass and a corresponding increase in DOC in water.

Conclusion

In the LTER site Istituto Mosso the C and N forms analyzed in soil and water for a decade showed a significant interannual variability, while a seasonal change was observed only for N-NO_3^- both in soil and water lake, with the greatest values recorded in early fall, probably due to the slowdown of biological-mediated processes of N immobilization.

Both the climatic and pedoclimatic conditions recorded during the snow-free and snow-covered season significantly influenced the C and N forms in soil and water. A little and delayed snowpack accumulation caused a high number of soil freeze/thaw cycles, which resulted in a high nitrate content both in soil and water. The longer the snow cover duration, the lower are all the soil C and N forms measured during the subsequent snow-free season, with the exception of DON. An opposite trend was observed for the lake water, where a longer snow-cover duration caused a higher content of inorganic N forms, probably due to a reduction in soil N immobilization potential.

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